



### Energy Focus

#### Rock-salt $\text{LiBH}_4$ phase solid electrolyte shows enhanced $\text{Li}^+$ conduction

From electric cars to consumer electronics, the demand for weight-efficient and sustainable energy storage is growing rapidly. Commercial lithium-ion batteries use a flammable liquid or gel electrolyte that is unsatisfactory for use in cars and have a limited charge-discharge cycle life due to dendrite formation at the electrode-electrolyte surface. Both of these issues could be solved by use of a solid electrolyte  $\text{Li}^+$  ion conductor. Indeed, some solid electrolytes have achieved room-temperature conductivities comparable to those of liquid/gel electrolytes, such as the garnets ( $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ,  $\text{M} = \text{Nb, Ta}$ ), where the La and M sites have substituted with other metals to “stuff” the structure with Li ions for conduction. However, there are still many problems to overcome before such solid electrolytes can be integrated into batteries, including sinterability, stability in contact with the Li metal anode, and the ability to make a chemically stable and conductively continuous interface with the cathode.

Now, a research team at Tohoku University in Japan has developed a new

method for achieving Li-ion conduction, as reported in the May issue of *APL Materials* (DOI: 10.1063/1.4876638). Their material is based on the normally high-pressure rock-salt phase of  $\text{LiBH}_4$ —a reducing agent familiar to organic chemists in its room-temperature orthorhombic phase—and which is stabilized by creating a solid solution between cubic KI and  $\text{LiBH}_4$ . This enables the rock-salt form of  $\text{LiBH}_4$  to be stabilized at ambient pressures.  $\text{LiBH}_4$  has good sinterability and stability in contact with Li metal, and its high-temperature tetragonal phase exhibits  $\text{Li}^+$  conductivities of 1 mS/cm, the minimum considered viable for consumer battery applications.

The solid solution has  $\text{Li}^+$  conductivities ranging from  $5 \times 10^{-3}$  S/cm at 145°C to  $10^{-7}$  S/cm at 21°C with an activation energy for conduction slightly higher than seen in other rock-salt  $\text{Li}^+$  conductors, consistent with the mixed-cation effect. “At this moment, we are working to enhance the ionic conductivity by optimizing a host material and composition,” said H. Takamura. The microstructure of the material, which was produced by sintering KI with  $\text{LiBH}_4$ , is a mix of rock-salt solid solution  $3\text{KI} \cdot \text{LiBH}_4$  and a secondary phase region which is K-deficient. The group

reports that  $\text{Li}^+$  migrates in the rock-salt grains through a vacancy-mediated conduction mechanism. A transference number near unity suggests that the material is a pure  $\text{Li}^+$  conductor, such that  $\text{K}^+$  remains immobile in the lattice.

It is unusual to see pure  $\text{Li}^+$  conduction in a solid solution so low in Li (<25 mol%) and which has completely stationary  $\text{K}^+$ . The researchers suggest that this occurs through a new phenomenon, which they term “parasitic conduction.” The light Li doping into the host lattice is sufficient for isotropic  $\text{Li}^+$  conduction. This may permit lithium electrolyte designers to propose systems previously considered inaccessible due to solubility limits.

“We believe that the ‘parasitic conduction’ of lithium ion is likely to happen in other systems such as oxides, sulfides, halides, and nitrides, if a small amount of lithium ion can be doped into the host materials. The concept opens the possibility of exploring new materials systems and/or crystal structures which have not been considered as a candidate for lithium ion conductors. We are working on that,” said Takamura.

**Jen Gordon**

### Breaking the 10-nm grain size barrier in ultrahard metals

High-strength metals are important for many mechanical applications such as wind energy turbines. Niels Hansen from the Department of Wind Energy at the Technical University of Denmark in Roskilde studies the microscopic phenomena and the atomic mechanical processes that determine or limit possible further strengthening of metals.

Refinement of the material microstructure is crucial for obtaining high-strength metals and is typically achieved by plastic deformation (e.g., cold-rolling). However, this is counteracted by a process of dynamic recovery. New

high strain deformation processes have enabled further structural refinement, resulting in nanoscaled Cu with boundary spacing down to an experimental limit of 10–20 nm. This was thought to be a theoretical barrier as well, as molecular dynamic simulations predicted a change from dislocation to grain-boundary sliding on that scale.

Now, as reported in the April 4 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.112.135504), Hansen and his collaborator, D.A. Hughes from Sandia National Laboratories in Livermore, Calif., describe an experimental method to surpass this limit. By alloying Cu with Fe, they show how the microstructure of Cu can be refined to a record low of 5 nm between boundaries.

To achieve this refinement, an extremely high strain (>150) was applied at a low sliding rate in liquid nitrogen.

The researchers also studied the evolution of the microstructure, and demonstrated that dislocation glide is still the limiting factor at this scale. With this observation, they then removed the expected theoretical limit. The researchers suggest that the presence of Fe, as well as a large density of dislocations, reduced the mobility of the boundaries and any possible dynamic recovery. The expected high strength suggests new potential applications in particular for hard wear-resistance materials—components that could make up the windmills of the future.

**Dirk Wouters**